## **EP95720**

**Publication Title:** 

Electrically conductive sintered ceramics and ceramic heaters

#### Abstract:

An electrically conductive sintered ceramics of the present invention comprises, as the main ingredients thereof, (a) silicon carbide, (b) an inorganic compound which exhibits a positive resistance-temperature coefficient, and preferably (c) a sintering assistant. The electrically conductive sintered ceramics obtained exhibits a positive resistance-temperature coefficient as a whole. A ceramic heater of the invention makes use of the electrically conductive sintered ceramics in an electrically conductive portion thereof. A sintered product which exhibits a positive resistance-temperature coefficient helps to prevent the occurrence of thermal runaway or thermal destruction.

Data supplied from the esp@cenet database - http://ep.espacenet.com

This Patent PDF Generated by Patent Fetcher(TM), a service of Stroke of Color, Inc.

11) Publication number:

**0 095 720** A2

12

## **EUROPEAN PATENT APPLICATION**

(2) Application number: 83105179.2

(5) Int. Cl.3: H 01 B 1/18, H 05 B 3/14

② Date of filing: 25.05.83

(30) Priority: 28.05.82 JP 89926/82

Applicant: HITACHI, LTD., 6, Kanda Surugadal 4-chome Chiyoda-ku, Tokyo (JP)

Date of publication of application: 07.12.83

Bulletin 83/49

Inventor: Matsushita, Yasuo, 2-2-15-304, Johnan-cho, Hitachi-shi Ibaraki-ken (JP) Inventor: Nakamura, Kousuke, 1-1-39, Ishinazaka-cho, Hitachi-shi Ibaraki-ken (JP) Inventor: Harada, Koji, 4-6-26, Higashitaga-cho, Hitachi-shi Ibaraki-ken (JP)

Designated Contracting States: DE FR GB

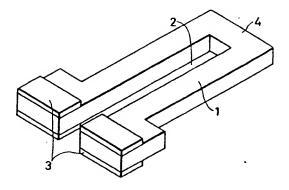
(A) Representative: Patentanwälte Beetz sen. - Beetz jun. Timpe - Slegfried - Schmitt-Fumian, Steinsdorfstrasse 10, D-8000 München 22 (DE)

Electrically conductive sintered ceramics and ceramic heaters.

An electrically conductive sintered ceramics of the present invention comprises, as the main ingredients thereof. (a) silicon carbide, (b) an inorganic compound which exhibits a positive resistance-temperature coefficient, and preferably (c) a sintering assistant. The electrically conductive sintered ceramics obtained exhibits a positive resistance-temperature coefficient as a whole.

A ceramic heater (1) of the invention makes use of the electrically conductive sintered ceramics in an electrically conductive portion thereof.

- A sintered product which exhibits a positive resistancetemperature coefficient helps to prevent the occurrence of thermal runaway or thermal destruction.



## TITLE OF THE INVENTION

ELECTRICALLY CONDUCTIVE SINTERED CERAMICS
AND CERAMIC HEATERS

#### BACKGROUND OF THE INVENTION

## FIELD OF THE INVENTION

5

The present invention relates to electrically conductive sintered ceramics and to ceramic heaters using these ceramics

#### DESCRIPTION OF THE PRIOR ART

Silicon carbide has an excellent hardness, strength 10 and resistance against oxidation and corrosion. It is also known that silicon carbide has a large resistance against impact under high-temperature conditions, owing to its small coefficient of thermal expansion and high heat conductivity. Silicon carbide with these 15 excellent characteristics is a promising material for a wide field of industrial applications such as engine parts for automobiles, turbine members, heat exchanger members, crucibles for melting metals, and jigs for use at high temperatures. In order to expand the 20 applications of silicon carbide, attempts have been made to blend silicon carbide with ceramics or intermetallic compounds to improve some characteristic of a sintered product of silicon carbide, or to impart new functions thereto. Examples of such studies are 25 disclosed in the specifications of U.S. Patent Nos.

3,875,476 and 3,895,219. The sintered products obtained by this prior art, however, have negative resistance-temperature coefficients and present the probability of being destroyed by heat.

Conventional glow plugs can be divided into those of the metal-sheathed type (indirect heating type) and the uncovered coil type (direct heating type).

A glow plug of the sheathed type is constructed by pouring a powder of a ceramic having a resistance against heat and heat conductivity, such as magnesium oxide powder, into and around the heat-producing coil in a metal tube. With a glow plug of the uncovered coil type, on the other hand, the heat-producing coil is exposed in the engine.

A glow plug of the former type is rigid and has a great durability against the combustion gases, but is poor in heat transmission, requires a time of longer than 5 seconds before the temperature on the surface of the sheath reaches the starting point, and hence lacks a rapid heating performance. Further, if attempts are made to increase the heating speed, the temperature of the heat-producing coil increases to close to the melting point of the heat-producing element to reduce its durability considerably. Therefore an upper limit of 950°C is imposed on the surface

temperature of the sheath. A glow plug of the latter type, on the other hand, can be heated rapidly, but the heat-producing element is subject to deterioration due to the combustion gases, and short-circuiting can easily develop due to the adhesion of carbon. From the standpoint of corrosion at high temperatures, furthermore, a temperature of 900°C may be the limit on the surface temperature of the heat-producing coil. Therefore, glow plugs of the sheath type are mainly used at the moment, despite their poor performance for rapid heating.

In recent years, however, an increasing demand had risen for diesel-engined automobiles to start as quickly as gasoline-engined automobiles. Under such circumstances, glow plugs of the direct heating type (surface hating type) have been reconsidered, and there is a strong desire to develop a heater element for glow plugs which can be heated quickly, and which has an excellent durability at high temperatures.

# 20 SUMMARY OF THE INVENTION

5

10

15

25

The object of the present invention is to provide an electrically conductive sintered ceramics which has an electric conductivity close to that of a metal, and provide a ceramic heater which is composed of the electrically conductive sintered ceramics

and which is free from being destroyed by heat.

The electrically conductive sintered ceramics of the present invention comprises (a) silicon carbide (SiC), (b) an inorganic compound having a positive resistance-temperature coefficient, and preferably (c) a sintering additive, as the main ingredients thereof, the sintered product exhibiting a positive resistance-temperature coefficient.

5

When a sintered product or inorganic compound having a positive resistance-temperature coefficient 10 is heated, its electrical resistance increases with temperature. If a sintered product has a negative resistance-temperature coefficient as do conventional products, the electrical resistance decreases with increasing temperature, and the current increases 15 under constant-voltage conditions. Namely, heat is produced spontaneously, the electrical resistance decreases correspondingly, and the current increases further, raising the probability of thermal runaway or thermal destruction. 2 o Therefore, if a sintered product exhibits a positive resistance-temperature coefficient, thermal runaway or thermal destruction can be prevented by using the sintered product in the electrically conductive part of a ceramic heater. In order for a sintered product to exhibit a positive 25

5

resistance-temperature coefficient, it is essential that component (b) has a positive resistance-temperature coefficient.

Examples of such a component (b) include zirconium boride (ZrB<sub>2</sub>) with a resistance-temperature coefficient of +1.76, titanium boride (TiB<sub>2</sub>) with a resistancetemperature coefficient of +2.78, molybdenum boride (Mo<sub>2</sub>B<sub>5</sub>) with a resistance-temperature coefficient of +3.3, zirconium silicate (ZrSi<sub>2</sub>) with a resistancetemperature coefficient of +2.65, molybdenum silicate (MoSi<sub>2</sub>) with a resistance-temperature coefficient of +6.38, tantalum silicate (TaSi2) with a resistancetemperature coefficient of +3.32, titanium nitride (TiN) with a resistance-temperature coefficient of +2.48, zirconium nitride (ZrN) with a resistancetemperature coefficient of +4.3, tantalumn carbide (TaC) with a resistance-temperature coefficient of +1.07, and zirconium carbide (ZrC) with a resistancetemperature coefficient of +0.95. A sintered product having the desired resistance characteristics can be 20 obtained even by adding metal powders. This, however, raises a difficulty concerning resistance to the oxidation at high temperatures, and the material obtained is not suitable in a heater for glow plugs.

The above examples of component (b) have melting points 25

of more than  $2000^{\circ}$ C and resistivities of less than  $10^{-4}$   $\Omega$  cm at room temperature.

According to the present invention, the electrically conductive sintered ceramic product should contain between 10 to 200 parts by weight of powder (b) for 100 5 parts by weight of powder (a). When the amount of component (b) is within this range, (1) the resistivity is less than 1  $\Omega$  cm, (2) the resistance-temperature coefficient becomes positive, (3) the sintered product 10 has an increased strength, and (4) an excellent resistance to oxidation is exhibited under hightemperature conditions. The sintering additive (c) should preferably be an aluminum compound or a boron compound, and a quantity of 0.1 to 3 % by weight should be used, based on the aluminum and/or boron content. Under this condition, (1) the relative density of the sintered product becomes as high as 85 % or higher of the theoretical density, and (2) there is no possibility of any increase in resistivity. particle diameter of powder (a) should preferably be 20 less than 10 µm.

According to the present invention, a mixture consisting chiefly of component (a), component (b), and preferably component (c) is pre-molded, and is then be sintered by hot-pressing in a non-oxidizing atmosphere

5

10

15

under the conditions of a temperature of between 1700° to 2300°C and a pressure of between 10 to 500 If the mixture is sintered in an oxidizing bar. atmosphere, the surfaces of the starting powders are oxidized, making it difficult to obtain a dense sintered product. If the hot-press sintering is effected at a temperature lower than 1700°C, it becomes difficult to obtain a dense sintered product having a relative density of more than 85 %. If the hot-press sintering is effected at a temperature higher than 2300°C, on the other hand, the mixture is sintered too much, giving rise to the occurrence of voids which reduce the strength. When the sintering temperature is within above range, hot pressing will usually be effected under a pressure of 10 to 500 bar, to obtain a very dense sintered product.

The thermal conductivity and thermal expansion coefficient of the silicon carbide type of composite ceramic material can be controlled by substituting

less for than 50 % by weight of component (b) one or more high melting point compounds having melting points of higher than 2000°C. If the additional components have melting points of more than 2000°C, the silicon carbide composite ceramic material

produced will not lose any hardness or strength under

high-temperature conditions. Further, when less than 50 % by weight of component (b) is replaced with an amount of other compounds, the silicon carbide composite ceramic material produced will lose its characteristics. More preferably, less that 30 % of component (b) should be replaced by of additional components.

5

10

15

25

The ceramic heater of the present invention is characterized in that the electrically conductive sintered ceramics is used for the electrically conductive member thereof, and is suitable for use in a heater of the direct heating type.

When studying heater materials of the direct heating type, the inventors of the present invention have discovered that a rapid heating performance can be achieved if the resistance of the heater is reduced to pass a heavy current instantaneously, that durability under high-temperature conditions can be accomplished if the heater is composed of a material containing compounds having high melting points and resistance to 20 oxidation, and that the heater material should have a positive resistance-temperature coefficient to prevent runaway of current when heat is produced and control the current easily so that the temperature on the surface of the heater is maintained constant because

of the resistance-temperature coefficient. Through extensive studies on heater materials having the above characteristics, the inventors have found that a silicon carbide composite sintered ceramic product has a low resistivity and a positive resistance-temperature coefficient, and exhibits durability in the high operating temperature ranges of a glow plug heater.

BRIEF DESCRIPTION OF THE DRAWINGS

5

15

Fig. 1 is a perspective view of a heater for a glow plug according to an embodiment of the present invention;

Fig. 2 is a diagram of the temperature-rise characteristics of the heater for a glow plug according to the embodiment of Fig. 1;

Fig. 3 is a diagram showing the changes of resistance during a current-carrying durability test using the heater for a glow plug according to the embodiment of Fig. 1; and

Fig. 4 is a diagram showing the changes of resistance during a high-temperature durability test using
the heater for a glow plug according to the embodiment
of Fig. 1.

# DESCRIPTION OF THE PREFERRED EMBODIMENTS

100 parts by weight of black SiC powder having
25 an average particle diameter of 10 μm was mixed with

2 parts by weight of Al<sub>2</sub>O<sub>3</sub> powder (1 % by weight based on the aluminum content) having an average particle diameter of 1 μm, and 80 parts by weight of ZrB<sub>2</sub> powder having an average particle diameter of 2 μm. The powder mixture was introduced into a metal mold and was molded under a pressure of 1000 bar. The molded product was introduced into dies of graphite, and was sintered by the hot-press method at a vacuum pressure of 1.3·10<sup>-3</sup> to 1.3·10<sup>-5</sup> mbar. The sintering was

effected under a pressure of 200 bar, while the temperature was raised from room temperature to 2050°C over a period of about 2 hours, was maintained at the temperature of 2050°C for one hour, and then the product was permitted to cool by turning off the

power supply. The pressure was reduced after the temperature had dropped to less than  $1500^{\circ}\text{C}$ . The thus obtained composite sintered product (SiC-ZrB<sub>2</sub>) had a relative density of 98 % (relative to the theoretical density of the composition), a bending strength

of about 50 N/mm<sup>2</sup> both at room temperature and at  $1300^{\circ}$ C, a thermal expansion coefficient of 42 x  $10^{-7}/{^{\circ}}$ C (between room temperature and  $1000^{\circ}$ C), a resistivity of 5 x  $10^{-4}$   $\Omega$  cm at room temperature, and a resistance-temperature coefficient of about +0.3 %/ ${^{\circ}}$ C

25 (between room temperature and 1000°C).

A cut-out 2 was formed in the thus obtained  $ZrB_2$ -SiC-type heater material 1 shown in Fig. 1 to obtain a U-shaped glow plug heater, and electrodes 3 were formed at both end portions A, B thereof by attaching a heat-resistant metal such as nickel, so that power-supply wires could be connected thereto. This heater was narrower at the U-shaped end 4, and hence generated the highest temperature at this portion. The heater material exhibited a resistivity of  $5 \times 10^{-4}~\Omega$  cm at room temperature, and a resistance of about 0.1 ohm across the electrodes A and B at room temperature.

Fig. 2 shows the results of heating speed measured by connecting the heater element of Fig. 1 to a d-c

15 power-supply circuit and by changing the voltage applied. The resistivity of the heater was 0.1 chm, the curve (i) represents the case when the temperature of the heater surface was 1200°C, and the curve (ii) represents the case when the temperature of the heater surface was 900°C. When a voltage of 12 volts, the same as that of a storage battery of a car, was applied, a temperature of 900°C was reached in about 0.7 second and a temperature of 1200°C was reached in about 1 second, this is considerably faster than the heating speed of

25 a conventional metal-sheathed heater (which takes 5

to 10 seconds before a temperature of 900°C is reached). When the heater surface was heated at 1000°C by passing an electric current therethrough, the heater resistance was about 0.3 ohm and hence it exhibited a positive resistance-temperature coefficient, providing a heater which is suitable for use in a glow plug.

5

10

15

20

25

Fig. 3 shows the changes of resistance (at room temperature) during a current-carrying durability test by repeated voltage-application cycles, each cycle consisting of applying a d-c voltage of 8 volts to the heater element of the embodiment of the invention for 2 seconds (the surface temperature reached about 1100°C after 2 seconds) and halting the flow of current for 30 seconds (the heater element was forcibly air-cooled during this period). In Fig. 3, the abscissa indicates the number of times the cycles were repeated. The resistance did not deteriorate at all even after a test of a hundred thousand cycles, and it was proved that the heater element possessed an excellent current-carrying durability and durability against intermittent heating to about 1100°C.

Fig. 4 shows the changes of resistance (at room temperature) during a high-temperature durability test in which heater elements of the embodiment of the invention were heat-treated in air at 900° to 1200°C

5

10

in an electric furnace. The curve (iii) shows the case when a heater element was heat-treated at  $1250^{\circ}$ C, a curve (iv) shows the case when a heater element was heat-treated at  $1200^{\circ}$ C, and a curve (v) shows the case when a heater element was heat-treated at  $900^{\circ}$ C,  $1000^{\circ}$ C and  $1100^{\circ}$ C. After heat-treatment for 2000 hours (which was considerably severer than the conditions encountered in practice in a vehicle), the resistance changed within + 5 % when the heater element was heat-treated at less than  $1200^{\circ}$ C, and by about + 10 % when if heat-treated at  $1200^{\circ}$ C, indicating the excellent du-ability of the heater element.

Thus, the electrically conductive sintered ceramic product according to the embodiment of the invention 15 has a low resistivity and hence a rapid heating performance as stated above. Further, owing to the positive resistance-temperature coefficient thereof. the electrically conductive sintered ceramic product is not melted by a runaway current even if it glows. Furthermore, the high melting point and resistance to 2 o oxidation thereof make the electrically conductive sintered ceramic product of the invention suitable for use as a heater member for a glow plug of the direct heating type for which a rapid temperature-raising 25 speed and durability at high temperatures are required.

The heater material according to the present invention has a high density, a low specific gravity and an increased strength (between room temperature and 1300°C). Therefore, the heater element can be constructed in a simple form such as rod, plate or U-shaped member. Using the heater material of the embodiment of the invention, therefore, a glow plug can be realized with a simple construction, a small size and a reduced weight when compared with existing metal sheathed glow plugs.

5

· 10

15

20

25

The present invention can be adapted not only to the heater of a glow plug, but also to a variety of heat-generating members, gas-igniting devices, heat-resistant conductors, electrically conductive spacers, and resistors.

According to the present invention as described above, a heater material of the direct heating type is provided which exhibits a rapid heating performance, an excellent durability at high temperatures, and which features a simple construction, small size and reduced weight.

Mixtures consisting chiefly of a powder of black silicon carbide having an average particle diameter of 1  $\mu m$  and a powder of component (b) having an average particle diameter of 5  $\mu m$ , were molded under a

pressure of 1000 bar, introduced into dies of graphite, and were sintered by a hot press at a vacuum pressure of  $1.3 \cdot 10^{-3}$  to  $1.3 \cdot 10^{-5}$  mbar. The sintering was effected under a pressure of 300 bar, the tempe-5 rature was raised from room temperature to 2050°C over a period of about 2 hours, it was maintained at  $2050^{\,\mathrm{O}}\mathrm{C}$  for 1 hour, and then the mixture was permitted to cool by turning off the power supply. The pressure was reduced after the temperature had dropped to below 1000°C. The thus obtained silicon carbide composite 10 sintered products, i.e., the electrically conductive sintered ceramic products according to the present invention, and their characteristics, are tabulated below.

Φ
ቯ
้๗
⊱

Resistivity (St cm)	4 x 10-4	$6 \times 10^{-3}$	8.0	6 x 10 <sup>-4</sup>	2 x 10 <sup>-4</sup>	1 x 10 <sup>-3</sup>	9 x 10 <sup>-4</sup>	1 x 10 <sup>-4</sup>	3 × 10 <sup>-4</sup>
Coefficient of thermal expansion. $(x 10^{-7})^{\circ}(c)$	50	87	5 <sup>1</sup> 7	817	24	. 09	617	24	87
Heat conductivity (W/m K)	87	82	79	80	81	78	76	98	93
Hardness HD $\frac{(N/mm^2)}{(N/mm^2)}$	30 000	29 000	27 000	28 000	29 000	29 000	27 000	26 000	25 000
Relative density (%)	91	66	95	76	92	. 36	. 26	91	93
Blend compo- sition (% by weight)	$sic-60\% TiB_2$	SiC-40% TiB2	SiC-20% TiB <sub>2</sub>	SiC-40% TiB <sub>2</sub> - 15% ZrB <sub>2</sub>	SiC-45% TiB <sub>2</sub> - 20% HfB <sub>2</sub>	SiC-40% TiB <sub>2</sub> -	SiC-40% TiB <sub>2</sub> - 10% ZrN	SiC-45% TiB <sub>2</sub> - 20% TaC	SiC-45% TiB <sub>2</sub> - 10% NbB <sub>2</sub>

	Resistivity ( \( \overline{\Omega} \) cm)	$2 \times 10^{-3}$	1 × 10 <sup>-3</sup>	7 × 10 <sup>-4</sup>	$2 \times 10^{-3}$	2 × 10 <sup>-3</sup>	3 x 10 <sup>-4</sup>	1 x 10-4	3 x 10 <sup>-3</sup>	0.1	9 x 10-5
(continued)	Coefficient of thermal expansion $(x 10^{-7})^{\circ}C)$	94	94	61	24	63	97	24	45	2 <sup>†</sup> 7	9†7
	Heat conductivity (W/m K)	06	86	29	71	69	88	68	70	73	72
Table	Hardness H <sub>D</sub>	25 000	25 000	24 000	31 000	27 000	25 000	26 000	25 000	24 .000	26 000 .
	Relative density (%)	. 76	76	96	95	26	92	66	93	26	98
	Blend composition (% by weight)	SiC-40% TiB <sub>2</sub> - 5% WC	SiC-40% TiB <sub>2</sub> - 5% MoB <sub>2</sub>	SiC-40% TiB <sub>2</sub> - 10% A-2 <sub>03</sub>	Sic-50% TiB <sub>2</sub> - 5% B <sub>4</sub> c	SjC-50% TiB2- 5% ZrO <sub>2</sub>	SiC-50% TiB <sub>2</sub> - 5% Si <sub>3</sub> N <sub>4</sub>	.sic-65% ZrB <sub>2</sub>	$SiC-40\% ZrB_2$	$sic-20\% zrB_2$	SiC-40% ZrB <sub>2</sub> - 20% HfB <sub>2</sub>

	Resistivity ( O cm)	2 x 10 <sup>-4</sup>	2 x 10 <sup>-4</sup>	1 × 10 <sup>-4</sup>	9 x 10-5	4 x 10-4	2 × 10-4	2 x 10 <sup>-4</sup>	3 × 10 <sup>-4</sup>
	Coefficient of thermal expansion $(x 10^{-7}/c)$	8 <sup>1</sup> 7	9†	24	94	- 24	94	51	77
(continued)	Heat conductivity (W/m K)	71	89	99	72	70	72	65	. 67
Table (co	Hardness $H_{\rm D}$ $(N/mm^2)$	28 000	25 000	27 000	26 000	24 000	23 000	24 000	25 000
	Relative density (%)	. 26	96	26	26	. 96	86	86	86
	Blend composition (% by weight)	SiC-40% ZrB <sub>2</sub> - 10% TiC	SiC-40% ZrB <sub>2</sub> - 15% ZrN	SiC-40% ZrB <sub>2</sub> - 15% TaB <sub>2</sub>	SiC-40% ZrB <sub>2</sub> - 10% NbC	S1C-40% ZrB <sub>2</sub> - 5% WC	SiC-50% ZrB <sub>2</sub> - 5% MoB <sub>2</sub>	SiC-45% 2rB <sub>2</sub> - 5% A 2 <sub>2</sub> 0 <sub>3</sub>	Sic-45% ZrB <sub>2</sub> - 5% B <sub>4</sub> C

(continued)	
Table	

											٠.
	Resistivity ( $\Omega$ cm)	4 × 10-4	1 x 10 <sup>-4</sup>	8 x 10-4	1 x 10-2	7.0	2 x 10-3	3 × 10 <sup>-3</sup>	6 x 10 <sup>-4</sup>	7 × 10 <sup>-4</sup>	5 x 10 <sup>-4</sup>
(continued)	Coefficient of thermal expansion $(x 10^{-7}/^{\circ}C)$	52	64	61	57	5 <sup>1</sup> 7	51	67	53	. 56	54
	Heat conductivity (W/m K)	29	71	81	79	22	92	62	. 70	72	84
Table (co	Hardness $H_{D}$ $(N / mm^2)$	24 000	25 000	24 000	23 000	22 000	21 000	22 000	23 000	24 000	24 000
	Relative density (%)	. 86	76	66	86	98	26	95	86	. 26	. 86
	Blend composition (% by weight)	SiC-50% ZrB <sub>2</sub> - 10% ZrO <sub>2</sub>	SiC-50% ZrB <sub>2</sub> - 5% Si <sub>3</sub> N <sub>4</sub>	Sic-60% TiN	SiC-40% TiN	S1C-20% TiN	SiC-30% TiN- 20% ZrN	SiC-30% TiN- 20% HfN	SiC-60% T1N- 25% ZrB <sub>2</sub>	SiC-60% TiN- 25% TiC	SiC-60% TiN- 25% TiB,

tinued)	
(conti	
Table	

		Table	(continued)		
Blend compo- sition (% by weight)	Relative density (%)	Hardness H <sub>D</sub>	Heat conductivity (W/m K)	Coefficient of thermal expansion $(x 10^{-7})^{\circ}C)$	Resistivity (
SiC-60% TiN- 10% TaN	. 76	23 000	81	52	4 × 10-4
SiC-50% TiN- 10% B <sub>4</sub> C	98	24 000	72	50	6 × 10 <sup>-3</sup>
SiC-50% TiN- 15% A.203	98	23 000	68	29	9 × 10 <sup>-3</sup>
SiC-40% TiN- 5% Si <sub>3</sub> N <sub>4</sub>	94	22 000	88	24	1 × 10 <sup>-2</sup>
SiC-40% TiN- 10% ZrO <sub>2</sub>	98	23 000	73	65	7 × 10 <sup>-2</sup>
SiC-40% TiN- 10% ZrC	26	22 000	71	54	6 x 10 <sup>-3</sup>
SiC-70% ZrN	96	22 000	72	45	6 × 10 <sup>-5</sup> .
Sic-50% ZrN	95	21 000	70	747	3 x 10 <sup>-4</sup>
SiC-20% ZrN	95	21 000	70	42	۲. o.
SiC-30% ZrN- 10% HfN	92	23 000	. 89	07	2 × 10 <sup>-3</sup>

	Resistivity ( $\Omega$ cm)	2 x 10 <sup>-4</sup>	4 x 10 <sup>-3</sup>	2.5 x 10 <sup>-4</sup>	7-01 x 7	$1 \times 10^{-2}$	0.1	8 × 10 <sup>-2</sup>	6 × 10 <sup>-2</sup>	4 x 10-3
	Coefficient of thermal expansion $(x 10^{-7}/^{\circ}C)$	97	67	77	43	. 07	56	. 04	53	7,7
Table (continued)	Heat conductivity (W/m K)	29	. 63	92	75	. 63	60	75	62	73
	Hardness H <sub>D</sub>	23 000	24 000	24 000	21 000	22 000	22 000	21 000	.21 000	21 000
	Relative density (%)	. 96	95	96	93	95	96	95	26	95
	Blend composition (% by weight)	SiC-40% ZrN- 10% ZrB <sub>2</sub>	SiC-30% ZrN- 10% TiC	SiC-35% ZrN- 15% TiB <sub>2</sub>	SiC-35% ZrN- 10% TaN	SiC-35% ZrN- 5% B <sub>4</sub> C	SiC-30% ZrN- 10% A4203	SiC-30% ZrN- 5% Si <sub>3</sub> N <sub>4</sub>	SiC-30% ZrN- 10% ZrO <sub>2</sub>	SiC-30% ZrN- 10% ZrC

As explained above, electrically conductive sintered ceramics of the above compositions have resistivities of smaller than 1  $\,\Omega$  cm.

### WHAT IS CLAIMED IS

- 1. An electrically conductive sintered ceramics, characterized in that it comprises, as the main ingredients thereof, (a) silicon carbide and (b) an inorganic compound which exhibits a positive resistance-temperature coefficient, said electrically conductive sintered ceramics exhibiting a positive resistance-temperature coefficient as a whole.
- 2. An electrically conductive sintered ceramics according to claim 1, characterized in that said component (b) is selected from titanium boride, zirconium boride, titanium nitride and zirconium nitride.
  - 3. An electrically conductive sintered ceramics according to claim 1, characterized in that the quantity of the
- 15 powder of said component (b) used is between 10 to 200 parts by weight for 100 parts by weight of the powder of said component (a).
  - 4. An electrically conductive sintered ceramics, characterized in that it comprises, as the main ingredients
- thereof, (a) silicon carbide, (b) an inorganic compound which exhibits a positive resistance-temperature coefficient, and (c) a sintering additive, said electrically conductive sintered ceramics exhibiting a positive resistance-temperature coefficient as a whole.
- 25 5. An electrically conductive sintered ceramics according to claim 4, characterized in that said component

- (c) is an inorganic compound selected from aluminium and boron compounds, and the quantity thereof in the starting materials mixture is between 0.1 to 3% by weight based on the aluminium or boron content.
- 6. An electrically conductive sintered ceramics according to claim 4, characterized in that the quantity of the powder of said component (b) used is between 10 to 200 parts by weight for 100 parts by weight of the powder of said component (a).
- 7. An electrically conductive sintered ceramics which exhibits a positive resistance-temperature coefficient as a whole, characterized in that it is obtained by hot-pressing and sintering a mixture composed, as the main ingredients thereof, of (a) silicon carbide,
- and (b) a ceramic material of the non-oxide-type other than silicon carbide, in a non-oxidizing atmosphere, at a temperature of between 1700° to 2300°C, under a pressure of between 10 to 500 bar.
- 8. A ceramic heater wherein an electrically conductive portion thereof is composed of an electrically conductive sintered ceramics, characterized in that it comprises, as the main ingredients thereof, (a) silicon carbide and (b) an inorganic compound which exhibits a positive resistance-temperature coefficient,
- 25 said electrically conductive sintered ceramics exhibiting a positive res\_istance-temperature coefficient as a whole.

- 9. A ceramic heater according to claim 8, characterized in that said electrically conductive sintered ceramics contains a sintering additive.
- 10. A ceramic heater according to claim 8 or 9,
  5 characterized in that the quantity of the powder of
  said component (b) used is between 10 to 200 parts
  by weight for 100 parts by weight of the powder of
  said component (a).

